Characterization of stability behavior of ultra fine alumina powder in view its colloidal processing by gel-casting

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ABSTRACT: The paper reports on the results of the study aimed at assessing of the influence of dispersant type on the electrochemical properties of highly concentrated alumina suspension. The relationship between the type of dispersant and the stabilization ability towards ultrafine alumina powder CT 3000 has been studied. The effectiveness was determined mainly by the zeta potential value, specific surface charge, the shift in the $pH_{(i.e.p.)}$ and by visual controlling the fluidity of the slurry at constant solid loading. A good agreement between the zeta potential and the specific surface charge as a way to determine the optimal dose of dispersant has been documented.

1 INTRODUCTION

The dispersion of ultra fine ceramic powders in aqueous media is of significant importance for the emerging direct consolidation techniques of ceramics processing. Gel casting is one of them, being especially advantageous with its ability to produce complex near net shape bodies with consistent properties and minimal defects. For realizing the process a well-dispersed suspensions with high solids loading are needed. This requires achieving strong stabilization of the suspension governed predominantly by steric of electrosteric mechanism. Prerequisite of steric stabilization of oxide ceramics is a strong adsorption of the dispersant onto the hydroxylic particle surfaces. Excellent recent studies and reports (Zücher and Graule, 2005; Hidber et al., 1997) have postulated four principal mechanisms for dispersant-powder interaction. The first one is ligand exchange, where the metal ion acts as a Lewis acid, which can exchange the coordinating hydroxyl group with the dispersant molecule, resulting in release of water molecule:

$$M\text{-}OH + H\text{-}L = M\text{-}L + H_20 \quad (1)$$

This mechanism is important in the presence of dispersant, which is able to form a chelate complex with the metal atom where two or more OH-groups are removed by one chelating molecule.

The second adsorption mechanism is ionic interaction under which the surface of the particle reacts with the dispersant, the charged dispersant molecule remains anchored to the particle surface by formation of an ionic bond:

$$H\text{-}L + HO\text{-}M = H_2L^+ . \ ^-O\text{-}M \quad (2)$$

The third way, is the molecule to adsorb by hydrogen bonding between the hydroxyl group of the particle surface and atoms of the dispersant molecule with non-bonding orbitals:

$$M\text{-}OH + B\text{-}R = M\text{-}O\text{-}H \ldots . |B\text{-}R \quad (3)$$

The last possibility to adsorb is through chemical adsorption. The dispersant reacts with the oxygen atom on the powder surface and forms a covalent bond while releasing a new molecule in solution.

The gel-casting process is based on development of liquid slurry containing colloidal sized ceramic powder and a predetermined amount of dispersant, gelling reagents, initiators and catalysts (Janney et al., 1988). Since the optimal dispersion of the particles and the stability of powder suspension is a key factor for development of desirable end products, the appropriate choice of dispersant type and its dose level above all, is by no doubts of primary importance for realizing a successful gel casting process. Often it is required to achieve as much as possible high solids loading in the slurry, since the high solids loading reduces the drying and sintering shrinkage and increases the green strength. There are various ways to select the dispersants, like for example studying suspension macroscopic properties such as sedimentation behavior and viscosity without considering the interfacial phenomena and particle-dispersant interactions.

Most often this is done on empirical basis, by time-consuming screening and performance evaluation (Singh et al., 2002). When the colloidal size range in particulate systems is concerned, the surface properties and interfacial phenomena determine to a large extent the state of particle dispersion. Hence the control over their dispersive behavior becomes increasingly difficult and sound information about surface and interfacial properties should be acquired.

The present paper reports on results from a systematic evaluation of the dispersive behavior of aqueous suspension of ultra fine alumina, stabilized by means of a four commercially available dispersants. The suspension stability has been assessed through measurement of its zeta potential and streaming current.

2 EXPERIMENTAL

2.1 *Materials*

A α-type calcined alumina powder CT 3000, obtained from Alcoa, Germany has been used. According to producer's data, it is characterized by a mean particle size of 0.8 μm and specific surface area (BET) of 8.32 m^2/g. For verification purposes, the suspended in water powder was subjected to particle size distribution measurement by the means of a DT 1200 spectrometer in acoustic attenuation mode, the results of which have indicated a mean size of 0.92 μm and bi-modal size distribution. One could notice a very good agreement between the measurement and the data coming from producer. The following cationic dispersants were used in course of the study: Dolapix CE 64 - an ammonium polyacrylate and Dolapix PC 75 - synthetic polyelectrolyte from Zschimmer & Schwarz, Germany and Darvan 7 and Darvan C - belonging to polymethacrylate group and supplied by R.T. Vanderbilt, USA. All have been used as 10 % solution and have been applied in concentration range between 1 and 24 mg/g. Unless otherwise stated, bi-distilled and de-ionised water from "Modulab" purification system with conductivity below 0.2 μS/cm and pH 6.7 has been used.

2.2 *Measurement of zeta potential and streaming current*

The electrokinetic properties of the alumina powder in suspension have been expressed as a zeta potential coming from measurement of the colloid vibration current (CVI) using an acoustic and electroacoustic spectrometer DT 1200, USA. The streaming current was measured by means a particle charge detector PCD-O3-pH, Mütek, Germany. The operational and measurement principles of the both systems are reported elsewhere (Duknin and Goetz, 2002; Wäsche et al., 2002). For the CVI tests, 5.5 grams of the powder have been added to 110 mL water, giving solids loading of 4.36 % W. The suspensions have been agitated for 2 minutes by magnetic stirrer, followed by 20 second with an ultrasonic disintegrator model UP400S, Dr Hilscher, Germany. Immediately after, they have been transferred inside the measuring chamber, where have been kept in circulation by the built-in magnetic stirrer. For estimation of the optimal dose of dispersant, two types of volumetric titrations have been performed. Firstly, the titration has been done using the CVI instrument, where a pre-determined amount of dispersant calculated on solid mass was added inside the chamber by means of the integrated burette and thoroughly mixed before zeta potential values have been taken. In the second approach using the PCD instrument, the powder-liquid mixing has been realised by the piston movement directly inside the 10 mL sample cell for 2 minutes, duration considered sufficient as indicated by establishment of a stable steaming current. Same level of solids loading as in the CVI tests has been maintained. A small pH electrode has been fitted to the cell, enabling on-line pH monitoring. For our purpose it was sufficient to follow progression of the streaming current only, however the exact magnitude of the charge expressed as specific surface charge or charge density could be also estimated, by titration with oppositely charged standard polyelectrolyte until neutralization of the streaming potential to zero value.

Thus, from the parallel studies, the optimum dispersant dose level leading to maximum powder dispersion has been considered as the one coinciding with the inflection point of the plots between dispersant dose level and zeta potential and between dispersant dose level and streaming current, as suggested by (Singh et al., 2003).

3 RESULTS AND DISCUSSION

3.1 *Comparison of dispersant effectiveness*

The results from the volumetric titration of the suspensions with different dispersants are summarized in Figure 1 and 2. For the CVI case, the dispersant was progressively dosed in a step-by-step addition mode directly inside a one and a same sample and accordingly each zeta potential value relates to measurement of the same sample. Each single point taken for the streaming current however, has been derived from measurement of an individual sample.

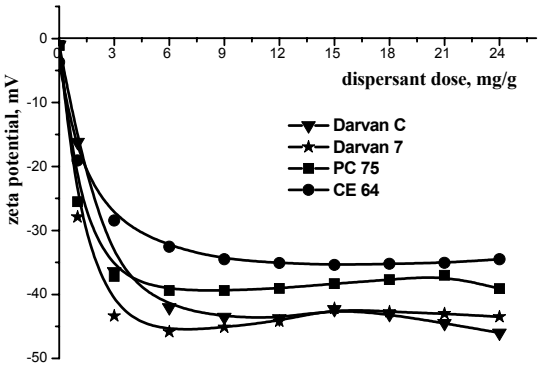

Figure 1. Zeta potential as function of dispersant dose levels for powder suspension in water

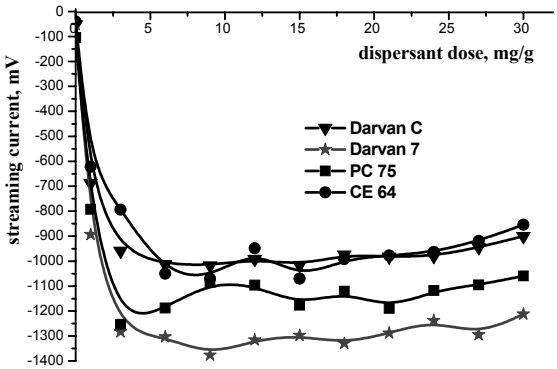

Figure 2. Streaming current as function of dispersant dose levels for powder suspension in water

As could be seen from Figure 1, without addition of dispersant the alumina-water suspension is almost neutrally charged and as such tends to agglomerate and settle in the suspension. Without dispersant addition, the suspension was characterized by pH of around 9. With increase in the amount of dispersant supplied, a negative zeta potential has emerged. For the different dispersants, the inflection point could be noticed at different dose levels, but for all of them, dosing further above that point leads to zeta potential curves flattening. As a rule, any amount of dispersant supplied above the optimum, will remain unbounded in suspension, leading to unwanted high viscosity. The optimum dispersant dose levels for the four dispersants could be estimated in the range 3 and 6.5 mg/g. Within this range, the zeta potential has reached absolute values higher than - 35 mV, which implies strong stabilization involving electrosteric mechanism. It has to be noted, that the progressive addition of dispersant within the envisaged range shifts the suspension pH to different extent. The dispersant with the lowest pH shift however was the CE 64. With this dispersant the pH has been found slightly decreasing from the natural value of 9.1 without dispersant, to about 8.9 at 18 mg/g. The rest of the studied dispersants, namely PC 75, Darvan C and Darvan 7 have shifted the pH respectively from 9.1 to 8.7, 8.8, 9.8 at 18 mg/g. The different degree of pH shift suggests a different dissociation pattern of the dispersants. It should be noted, that only the Darvan 7 has provided an increase in suspension pH towards alkaline region. Figure 2 shows the volumetric titration performed with the PCD instrument, linking the streaming current with the dispersant dose. It could be noted, that likewise to the zeta potential study, a similar trend in the behavior of the four studied dispersants could be observed.

The results from the both volumetric titrations (CVI and PCD) shown at Figures 1 and 2 suggest, that on comparative basis Darvan 7 has provided the maximum charge loading, while the CE 64 could be viewed as the one with the lowest charging power among the studied dispersants. Regardless of the different modes used for dispersant introduction inside the suspension, during the CVI and streaming current determination, the trends in the zeta potential and specific surface charge curves are quite similar. Therefore, it could be postulated that the optimal dose levels of dispersant suggested by the zeta potential measurement are in good agreement with those obtained from the streaming current. Table 1 summarizes the assumed optimal dose levels required for maximum stabilization of the suspension and the respective zeta potential values measured at the optimal dose level.

3.2 *Shift in suspension* $pH_{(i.e.p.)}$

The ability of the dispersants to shift the suspension pH of iso electric point is an important characteristic and indication about the their presumed adsorption pattern and deflocculating ability. Therefore, it was further important to evaluate up to which extent a shift in the $pH_{(i.e.p.)}$ is to be expected for each of the dispersants supplied at their optimal dose level. Figure 3 illustrates the results coming from this direction, i.e. from the potentiometric titration, linking the suspension pH and zeta potential.

Table 1. Optimal dose level of the dispersants as indicated by the volumetric titration and zeta potential values at the optimal dose level

Dispersant	Dose, mg/g	ξ, mV
CE 64	6.5	- 35
PC 75	6	- 39
Darvan 7	6	- 46
Darvan C	9	- 43

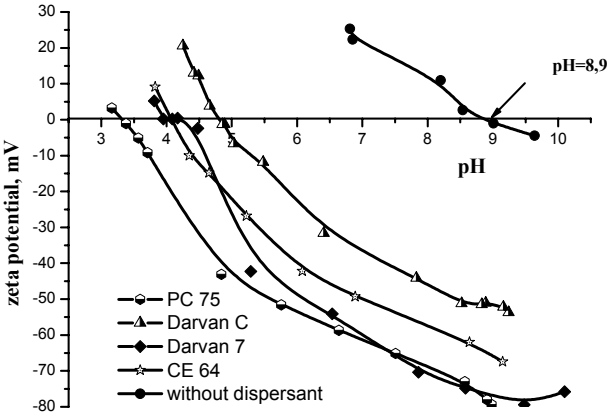

Figure 3. Relationship between zeta potential and pH of suspension treated with optimal concentration of dispersant and shift in suspension $pH_{(i.e.p.)}$ as result of dispersant addition.

A perusal of the results shown at Figure 3 indicates, that without addition of dispersant the pH of iso electric point is about 8.9. All the studied dispersants have shifted the $pH_{(iep)}$, fact which suggests they do adsorb onto particle surface through involvement of chemical sorption as well. A different degree of shift in $pH_{(i.e.p.)}$ could be observed however, the dispersant with the larger shift being PC 75 – shift to pH 3.3 followed by the CE 64 and Darvan 7 – shift to pH 4. Darvan C has provided the lowest shift in $pH_{(i.e.p.)}$ – shift to pH 4.8. The observed deviation in the $pH_{(i.e.p.)}$ shifts, most likely should be attributed to differences in the intrinsic chemical structure of the dispersants.

Since the zeta potential values of the suspension pertinent to each dispersant and the respective shift in $pH_{(i.e.p.)}$, are not sufficient to fully characterize their dispersion ability in case of practical scenarios, the decision about the best dispersant system, should be done only after performing the inevitable studies regarding stabilization ability under higher solid loadings, similar to the one required in the gel-casting process. This is because not every dispersant which provides good stabilization at lower solids loading, shows the same stabilizing performance and maintains low viscosity at higher solids loading. Studies in this direction are already underway.

4 CONCLUSIONS

Based on the presented results, the following conclusion could be derived.

An acceptable agreement between the optimum dose level of dispersant required to stabilize a water suspensions of alfa alumina powder by four different dispersant could be noted, as indicated by the zeta potential values coming from the CVI and the streaming current values derived from the PCD measurements.

The tested dispersants for the powder under consideration possess different functional groups which provide various degree of surface charging of alumina surface, but all of them attach with involvement of certain degree of chemical sorption.

For final evaluation of the best dispersant system and proving the suggested optimal dose levels, further studies at higher solids loading of powder usually employed in practical gel casting processes, should be performed, supplemented by viscosity and rheology measurements as well.

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